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PHOTOCHEMICALLY GENERATED SILICON-CARBON DOUBLE-BONDED INTERMEDIATES

VI. THE REACTION OF PHENYL AND *p*-TOLYLPENTAMETHYLDISILANES WITH ALKYNES

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Summary

The reaction of photochemically generated silicon-carbon double-bonded intermediates produced from phenyl- and *p*-tolylpentamethyldisilane with alkynes is described. The reaction of the silicon-carbon double-bonded intermediates with 1-hexyne and trimethylsilylacetylene gave (*E*)-1-(*o*-trimethylsilyl)aryldimethylsilyl-1-hexene and (*E*)-1-(*o*-trimethylsilyl)aryldimethylsilyl-2-trimethylsilylethene, respectively. With phenylacetylene and bis(trimethylsilyl)acetylene, both (*Z*)- and (*E*)-adducts were obtained. Acetylene itself also reacted with the reactive intermediate to give the corresponding adduct. The formation of these products can be best rationalized in terms of a mechanism involving radical species.

Introduction

There have been very rapid developments within the last few years in the chemistry of silicon-carbon double-bonded intermediates [1]. It has been shown that these intermediates react with various substrates such as alcohols [2-6], ketones [7,8] and olefins [9,10] to give the corresponding adducts. However, to our knowledge, there have been no reports concerning the reaction of such intermediates with alkynes.

Recently we showed that the silicon-carbon double-bonded intermediates (A) (see Scheme 1) generated by photolysis of aryldisilanes readily add to the unsaturated compounds such as olefins [10a], dienes [10b] and carbonyl compounds [11] to afford addition products whose formation can be best rationalized in terms of a mechanism involving radical species in the addition step. In order to obtain further information concerning the mechanism in the reaction of intermediates A with unsaturated compounds, we examined the photolysis of aryldisilanes in the presence of compounds having a carbon-carbon triple bond. We report here evidence that the present results support the formation of biradical species in the addition step.

Results and Discussion

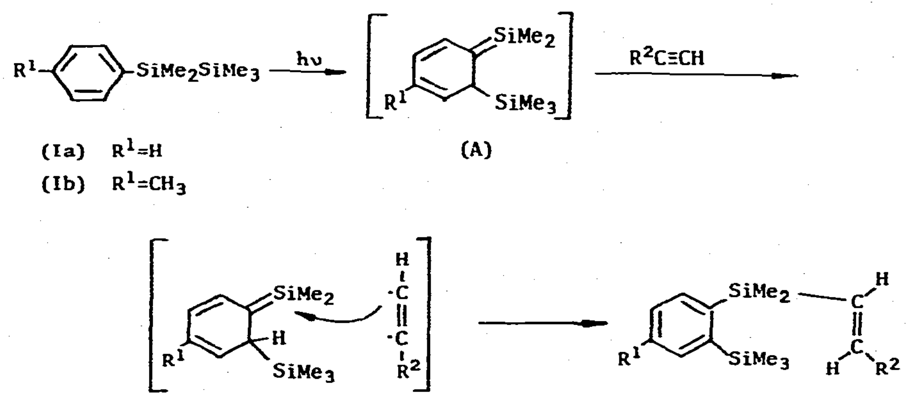
The photochemical studies were carried out using a low-pressure mercury lamp with a Vycor filter (2537Å). Irradiation of phenylpentamethyldisilane (Ia) in the presence of a large excess of 1-hexyne in benzene under a purified nitrogen atmosphere for 10 h with ice-cooling was found to afford (*E*)-1-[(*o*-trimethylsilylphenyl)dimethylsilyl]-1-hexene (II) in 21% yield as a major product (Scheme 1), in addition to 9% combined yield of two geometric isomers of 3-(1-n-butyl-2-trimethylsilyl)vinyl-1-sila-2,4,6-cycloheptatriene (a substituted silepin) [12]. The stereochemical assignment of II was based on the coupling constant of the olefinic protons (J=18.7 Hz).

Photolysis of Ia in the presence of trimethylsilylacetylene in benzene under the same conditions, again, gave an (*E*)-olefin (III) (J=22.6 Hz) in 15% yield as the sole product. Also, irradiation of *p*-tolylpentamethyldisilane (Ib) in the presence of 1-hexyne in benzene gave an adduct (23% yield) whose structure, (*E*)-1-[(*o*-trimethylsilyl)(*p*-methyl)phenyldimethylsilyl]-1-hexene (IV), could be assigned on the basis of its NMR spectrum (J=18.5 Hz), in addition to 12% yield of the silepin analogous to that mentioned above [12].

Seyferth and Vaughan [13] have reported that (*Z*)- and (*E*)-propenyltrimethylsilane undergo photoisomerization upon irradiation with UV-light to give an equilibrium mixture consisting of the *Z* and *E* isomers in a ratio of 19/81. However, in our system, no isolable amounts of the *Z* isomer (less than 3%) were produced from the photolysis of I in the presence of either 1-hexyne or trimethylsilylacetylene. Furthermore, irradiation of the isolated pure compounds, II-IV, in benzene at 2537Å for 10 h led to approximately 90% decomposition of the starting compounds, giving mainly non-volatile substances. Again, no *Z* isomers were detected.

The quenching ability of the acetylenic compounds seems lower than that of olefins or dienes which gave the adducts in high yield. In all cases, non-volatile products arising from polymerization of intermediate A were observed after distillation of the reaction mixture. Fig. 1 illustrates observed yields of products vs time for the photolysis of Ia in the presence of 1-hexyne as a typical example.

Scheme 1



(Ia) R^1=H
(Ib) R^1=CH_3

(A)

(II) R^1=H, R^2=n-Bu
(III) R^1=H, R^2=Me_3Si
(IV) R^1=CH_3, R^2=n-Bu
(V) R^1=R^2=H

Non-substituted acetylene also reacted with intermediate A at room temperature to give an adduct (V) as a single volatile product in low yield.

The yields and ^1H NMR data for the adducts reported here are listed in Tables 1 and 2.

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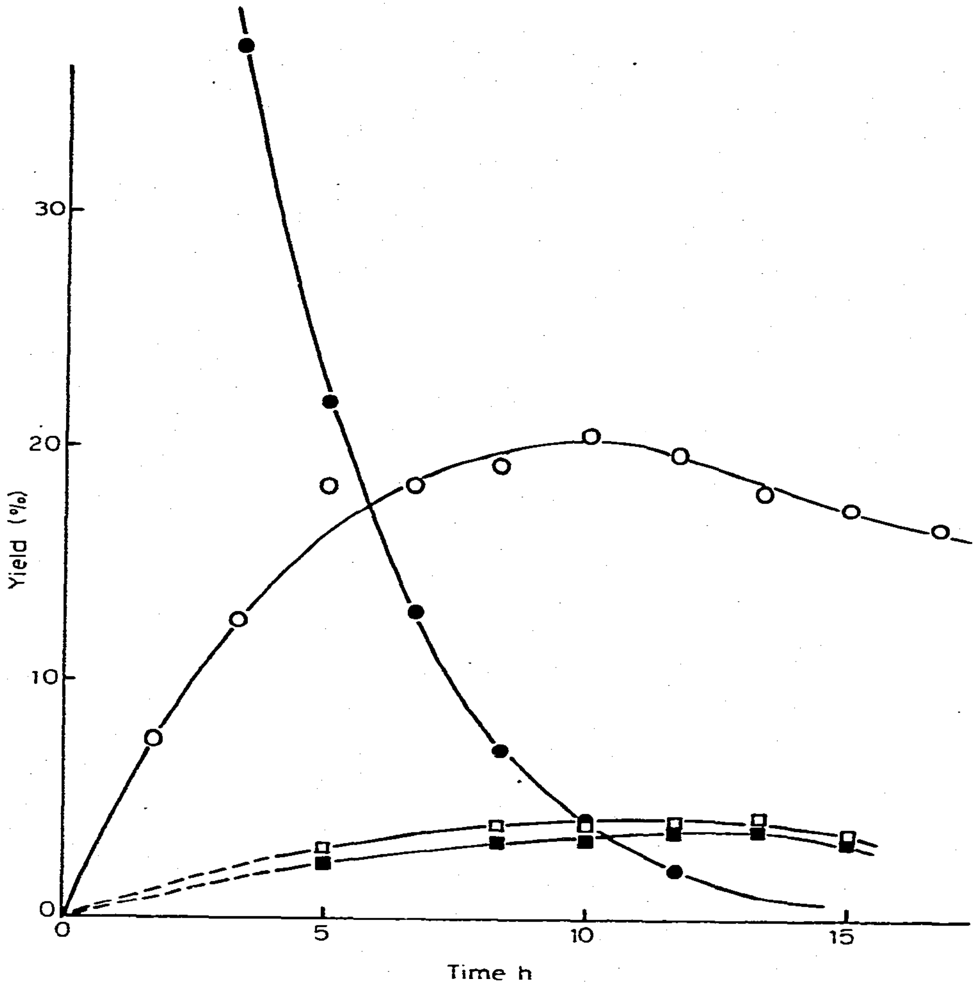


Fig. 1. Photolysis of phenylpentamethyldisilane in the presence of 1-hexyne. ●, Ia; ○, II; ■ and □, silepins.

TABLE 1

REACTION CONDITIONS AND ANALYTICAL DATA FOR ISOLATED COMPOUNDS

Aryldisilane g (mmol)	RC≡CR g (mol)	Time (h)	Yield of product (%)	Recovered aryldisilane (%)	Formula	C (%) found (calcd.)	H (%) found (calcd.)
$PhMe_2SiSiMe_3$ 0.9810 (4.71)	n-BuC≡CH 16 (0.20)	10^b	II (21)	5	$C_{17}H_{30}Si_2$	70.45 (70.26)	10.60 (10.41)
$PhMe_2SiSiMe_3$ 0.9613 (4.61)	$Me_3SiC≡CH$ 5 (0.051)	10^b	III (15)	8	$C_{16}H_{30}Si_3$	62.72 (62.66)	9.85 (9.86)
$CH_3C_6H_4SiMe_2SiMe_3$ 0.9910 (4.45)	n-BuC≡CH 16 (0.20)	10^b	IV (23)	8	$C_{18}H_{32}Si_2$	70.77 (70.97)	10.45 (10.59)
$PhMe_2SiSiMe_3$ 0.9850 (4.73)	$HC≡CH^a$	3.5^c	V (7)	5	$C_{13}H_{22}Si_2$	66.70 (66.59)	9.59 (9.46)
$PhMe_2SiSiMe_3$ 0.9510 (4.56)	$Me_3SiC≡CSiMe_3$ 5 (0.029)	10^b	(*E*)-VIa (5) (*Z*)-VIb (4)	4	$C_{19}H_{38}Si_4$	60.48 60.53 (60.24)	10.05 9.92 (10.11)
$PhMe_2SiSiMe_3$ 1.0006 (4.80)	PhC≡CH 0.5062 (4.96×10^{-3})	10^c	(*Z*)-VII (12) (*E*)-VII (13)	22	$C_{19}H_{26}Si_2$	73.53 73.46 (73.48)	8.68 8.56 (8.44)

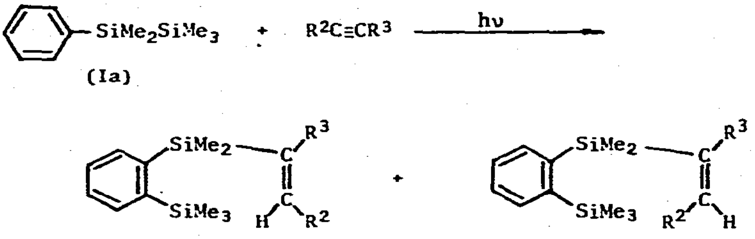
[a] Photolysis was carried out under bubbling dry acetylene. [b] With ice cooling. [c] At room temperature.

TABLE 2

^{1}H NMR AND MOLECULAR WEIGHT DATA FOR ISOLATED ADDUCTS

Compound	Chemical shift (δ) in CCl_4	M^+
II	0.30(CH_3-$SiMe_2$, s, 9H), 0.37(CH_3-SiMe, s, 6H), 0.90(CH_3-C, m, 3H), 1.38(-CH_2-CH_2-, m, 4H), 2.14(-CH_2-C=C, m, 2H), 5.81(C=CH-Si, d, 1H, J=18.7 Hz), 5.99(C=CH-Bu, dt, 1H, J=18.7 Hz, J=5.0 Hz), 7.10-7.64(ring protons, m, 4H)	290
III	0.08(CH_3-$SiMe_2$C=C, s, 9H), 0.32(CH_3-$SiMe_2C_6H_4$, s, 9H), 0.41(CH_3-$SiMeC_6H_4$, s, 6H), 6.60(vinyl proton, d, 1H, J=22.6 Hz), 6.80(vinyl proton, d, 1H, J=22.6 Hz), 7.19-7.63(ring protons, m, 4H)	306
IV	0.28(CH_3-$SiMe_2$, s, 9H), 0.33(CH_3-SiMe, s, 6H), 0.91(CH_3-C, m, 3H), 1.36(-CH_2-CH_2-, m, 4H), 2.13(CH_2-C=C, m, 2H), 2.31(CH_3-C_6H_3, s, 3H), 5.79(C=CH-Si, d, 1H, J=18.5 Hz), 5.96(C=CH-Bu, dt, 1H, J=18.5 Hz, J=5.0 Hz), 7.02(ring proton, broad d, 1H, J=7.8 Hz), 7.35(ring proton, broad s, 1H), 7.43(ring proton, d, 1H, J=7.8 Hz)	304
V	0.32(CH_3-$SiMe_2$, s, 9H), 0.41(CH_3-SiMe, s, 6H), 6.02(vinyl protons, m, 3H, J_{trans}= 19.5 Hz, J_{cis}=14.6 Hz, J_{vic}=4.6 Hz), 7.15-7.60(ring protons, m, 4H)	234
(*E*)-VIa	0.04(CH_3-$SiMe_2$, s, 9H), 0.14(CH_3-$SiMe_2$, s, 9H), 0.29(CH_3-$SiMe_2$, s, 9H), 0.42 (CH_3-SiMe, s, 6H), 7.28(vinyl proton, s, 1H), 7.16-7.62(ring protons, m, 4H)	378
(*Z*)-VIb	-0.06(CH_3-$SiMe_2$, s, 9H), 0.03(CH_3-$SiMe_2$, s, 9H), 0.33(CH_3-$SiMe_2$, s, 9H), 0.48 (CH_3-SiMe, s, 6H), 7.36(vinyl proton, s, 1H), 7.15-7.64(ring protons, m, 4H)	378
(*Z*)-VII	0.28(CH_3-SiMe, s, 6H), 0.31(CH_3-$SiMe_2$, s, 9H), 6.06(vinyl proton, d, 1H, J=15.1 Hz), 7.04(ring protons, s, 5H), 7.16-7.29(ring protons, m, 2H), 7.34(vinyl proton, d, 1H, J=15.1 Hz), 7.51-7.64(ring protons, m, 2H)	310
(*E*)-VII	0.32(CH_3-$SiMe_2$, s, 9H), 0.49(CH_3-SiMe, s, 6H), 6.59(vinyl proton, d, 1H, J=19.3 Hz), 6.82(vinyl proton, d, 1H, J=19.3 Hz), 7.13-7.66(ring protons, m, 9H)	310

In order to obtain further information as to the stereochemistry of the reaction, we photolyzed Ia in the presence of a large excess of bis(trimethylsilyl)acetylene under similar conditions. Interestingly, two geometric isomers (VIa and VIb) easily separable by preparative GLC were produced in a ratio of 56/44. The structures of both isomers were determined by mass and NMR spectroscopic analyses. The proton NMR spectrum of isomer VIb showed an upfield shift for the trimethylsilyl group attached to the terminal unsaturated carbon. The additional shielding is attributed to the ring current of the silyl-substituted aromatic ring *cis* to this trimethylsilyl group and therefore we assign the *Z* structure to VIb and the *E* structure to VIa. Photolysis of a 1/1 mixture of Ia and phenylacetylene in benzene at room temperature for 10 h, again, gave two isomers, (*E*)- and (*Z*)-β-(*o*-trimethylsilylphenyl)dimethylsilylstyrene (VII), in a ratio of 52/48. It was thought that one isomer might be produced from photoisomerization of the other which was initially formed. Indeed, irradiation of a pure sample of *E* isomer (VIa) in benzene for 5 h gave an equilibrium mixture of *E* and *Z* isomers in a ratio of 53/47. Attainment of the true equilibrium was confirmed by the observation that the same ratio of *E* to *Z* isomer is also obtained by photolysis of the pure *Z* isomer (VIb). Similarly, irradiation of either (*E*)-VII or (*Z*)-VII in benzene for 6 h under the same conditions gave an equilibrium mixture. In this case, the ratio of *E* to *Z* isomer was observed to be 39/61 (see Fig. 2). In contrast to II-IV, compounds VI and VII did not lead to any polymeric substances after 15 h irradiation.



(Ia)

(VIa) $R^2=R^3=SiMe_3$
(*E*)-(VII) $R^2=Ph$, $R^3=H$

(VIb) $R^2=R^3=SiMe_3$
(*Z*)-(VII) $R^2=Ph$, $R^3=H$

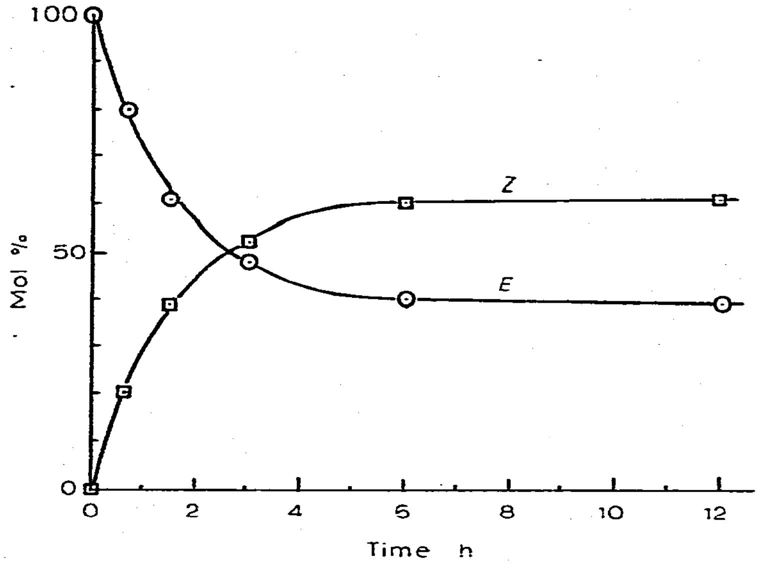


Fig. 2. Photoisomerization of (*E*)-(*o*-Me_3Si-C_6H_4)$SiMe_2CH=CHPh$

In order to establish whether or not some of the *Z* isomer was produced as an initial product in the photolysis of Ia in the presence of phenylacetylene, we followed the progress of the reaction by GLC. Fig. 3 illustrates a profile for the formation of *Z* and *E* isomers as a function of time. Extrapolation of the curve for *E*/(*Z*+*E*) vs time to t=0 does not lead to an intercept at 100% *E*. A similar result was obtained for the photolysis of Ia in the presence of bis(trimethylsilyl)acetylene. This definitely indicates that all of the *Z* isomer is not a secondary product arising from the photoisomerization of the *E* isomer.

Consequently, the *Z* isomer must be formed simultaneously by two independent pathways: One involves the direct formation in the addition step of reactive intermediate A to phenylacetylene, the other is the photoisomerization of the *E* isomer.

Recently, Ingold and co-workers reported an EPR study of various silyl-substituted vinyl radicals [14]. Their conclusion is that among them the $Me_3Si\dot{C}=C(SiMe_3)_2$ radical alone is truely linear like the vinyl radicals

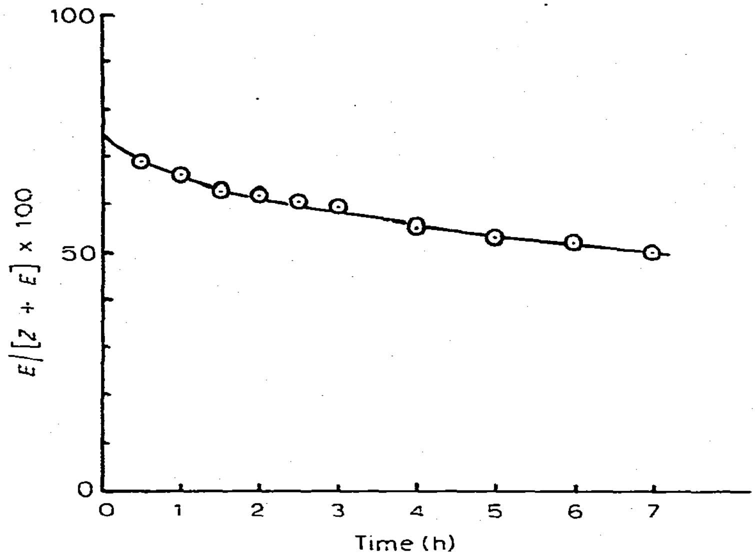
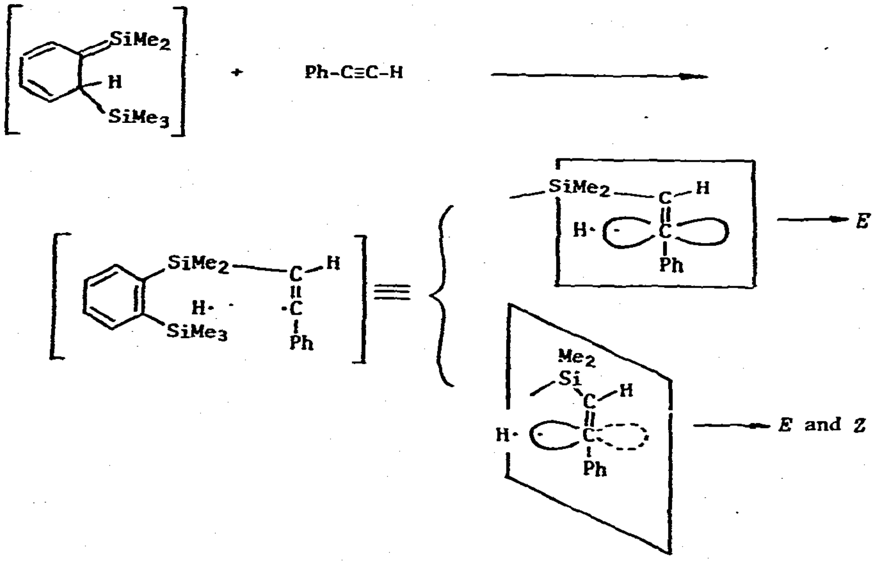


Fig. 3. Relationship of the formation of (*E*)- and (*Z*)-(o-Me_3Si-C_6H_4)$SiMe_2CH$=$CHPh$ vs Time

having an α substituent, such as the phenyl group, capable of delocalizing the unpaired electron; others are of bent structure.

The initial formation of both *E* and *Z* isomers in the photolysis of Ia in the presence of bis(trimethylsilyl)acetylene or phenylacetylene can be best understood in terms of a mechanism involving radical species. Thus, the silicon-carbon double-bonded intermediate A reacts with bis(trimethylsilyl)acetylene and phenylacetylene yielding the vinyl radical species which can be expected to have the linear structure. Presumably, these radicals undergo intramolecular hydrogen abstraction to give both *E* and *Z* isomers. The reaction of intermediate A with phenylacetylene is shown in Scheme 2 as a typical example.

Scheme 2



Experimental

Materials. Trimethylsilylacetylene [15] and bis(trimethylsilyl)acetylene [16] were prepared in the standard manner by the reaction of $CH\equiv CMgBr$ and $BrMgC\equiv CMgBr$ with trimethylchlorosilane, respectively. Benzene used as solvent was treated with concentrated sulfuric acid, refluxed over sodium, and distilled. The distillate was dried over lithium aluminum hydride and distilled from it just before use.

Photolysis of aryldisilanes in the presence of alkynes

The following is typical of the procedures used. In a reaction vessel, fitted internally with a low-pressure mercury lamp having a Vycor filter, a solution of 0.9810 g (4.71 mmol) of Ia and 16 g (0.20 mol) of 1-hexyne in 100 ml of dry benzene was irradiated for 10 h under bubbling nitrogen. Most of the benzene was evaporated and the residue was distilled under reduced pressure. The yield of the product contained in the distillate was determined by GLC using n-eicosane as an internal standard.

Pure compounds were isolated by preparative GLC. All the isolated products were colorless liquids. The yields, reaction conditions and analytical data for isolated products are listed in Table 1.

Photochemical isomerization of (E)- and (Z)-VI and (E)- and (Z)-VII

In a carefully dried quartz test-tube was placed a solution of an exactly weighed sample of VI or VII and a known quantity of n-eicosane as an internal standard in benzene. The following are the quantities used of pure *E* and Z isomers, n-eicosane (shown in parenthese) and benzene: for VIa, 28 mg (8 mg) 5 ml; for VIb, 32 mg (10 mg) 5 ml; for (*E*)-VII, 9.5 mg (5.1 mg) 1.0 ml; for (Z)-VII, 15.8 mg (9.1 mg) 1.5 ml. The solution was purged with dry nitrogen and the tube was sealed with a serum cap. It was then irradiated externally with a low-pressure mercury lamp with a Vycor filter at room temperature. At suitable intervals small aliquots of the solution were extracted through the serum cap by means of a micro syringe and analyzed by GLC. The results from (*E*)-VII are illustrated in Fig. 2 as a typical example.

Photolysis of Ia in the presence of phenylacetylene in benzene

In a similar quartz tube to that used above was placed a mixture of 76 mg (0.37 mmol) of Ia, 28 mg (0.27 mmol) of phenylacetylene and 12 mg of n-eicosane dissolved in 5 ml of dry benzene. The mixture was irradiated externally with ultraviolet light and small aliquots of the solution were analyzed by GLC at suitable intervals. The results are shown in Fig. 3.

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